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STUDY OF THE SOLUBILITY OF RADIUM-226 IN SULFATE MEDIA

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Summary

The sulfate salts of barium, lead and calcium have been prepared and doped with varying concentrations of radium-226. These radium-226 labelled salts have then been subjected to a series of experiments to measure how much radium-226 dissolves as a function of such variables as pH, sulfate concentration and ferrous iron concentration. Other experiments were conducted to examine whether radium-226 will coprecipitate with ferric hydrous oxide under a variety of conditions. The ferric hydrous oxide precipitates were subjected to a series of sequential chemical extractions to determine whether any radium-226 coprecipitated and if so, the degree of tenacity with which it was held.

The results of these experiments have shown that the solubility of radium-226 varies considerably amongst the three metal sulfate salts. One important discovery is that radium-226 does not always dissolve in direct proportion to the solubility of the host matrix. This observation is of significance in the development of mathematical models. Another important discovery is that radium-226 will coprecipitate with ferric hydrous oxide in significant quantities. Other tests show that this radium-226 can also be subsequently solubilized once again.

Table of Contents

	Page
Title Page	i
Summary	ii
Table of Contents	iii
List of Figures	iv
List of Tables	v
1. Introduction	1
2. Experimental	
2.1. Preparation of Ra-226 Labelled Sulfate Salts of Calcium, Lead and Barium	2
2.1.1. Preparation of Ra-226 Labelled Calcium Sulfate	
2.1.2. Preparation of Ra-226 Labelled Lead Sulfate	
2.1.3. Preparation of Ra-226 Labelled Barium Sulfate	
2.2. Analysis of Ra-226 Labelled Sulfate Salts of Calcium, Lead and Barium	3
2.3. Studies to determine Time Required for Equilibrium	4
2.4. Solubility of Labelled Metal Sulfates as a Function of pH	4
2.5. Solubility of Labelled Metal Sulfates as a Function of Sulfate Concentration	4
2.6. Solubility of Labelled Metal Sulfates as a Function of Ferrous Iron Concentration at pH 3.5	5
2.7. Precipitation of Ferric Hydrous Oxide	5
2.8. Sequential Extraction of Ferric Hydrous Oxide Samples	5
3. Results and Discussion	17
4. References	21
5. Acknowledgements	21

List of Figures

Figure	Title
1	Release of Ra-226 from Calcium Sulfate as a Function of pH
2	Release of Ra-226 from Lead Sulfate as a Function of pH
3	Release of Ra-226 from Barium Sulfate as a Function of pH
4	Release of Ra-226 from Calcium Sulfate as a Function of Sulfate Concentration
5	Release of Ra-226 from Lead Sulfate as a Function of Sulfate Concentration
6	Release of Ra-226 from Barium Sulfate as a Function of Sulfate Concentration

List of Tables

Table	Title
1	Analysis of Ra-226 Labelled Sulfate Salts of Calcium, Lead and Barium
2	Concentrations of Metal Sulfates during Equilibration at pH 4
3-1	Solubility of Ca(Ra-226)SO4 for the Intermediate Ra-226 Activity as a Function of pH
3-2	Solubility of Pb(Pb-210,Ra-226)SO4 for the Intermediate Ra-226 Activity as a Function of pH
3-3	Solubility of Ba(Ba-133,Ra-226)SO4 for the Intermediate Ra-226 Activity as a Function of pH
3-4	Solubility of Metal Sulfates containing High, Intermediate and Low Activities of Ra-226 at pH 4
4	Solubility of Metal Sulfate Salts containing Intermediate Ra-226 Activity Levels as a Function of Sulfate Concentration at pH 4
5	Solubility of Metal Sulfate Salts containing Intermediate Ra-226 Activity Levels as a Function of Ferrous Iron Concentration at pH 3.5
6	Mass of Ferric Hydrous Oxide Precipitates
7	Sequential Extraction of Ferric Hydrous Oxide for Ra-226

1. Introduction

The National Uranium Tailings Program is developing mathematical models to predict future events pertaining to uranium tailings and to quantify and assign uncertainties to these predictions. To do so, data and information on the pathways of release of contaminants from the tailings in the long term are being obtained. Radium-226 is the major radioactive contaminant in the tailings and its physical nature and ensuing reaction pathways must be well defined. Previous work has suggested that the solubility, and consequently the mobility, of Ra-226 in uranium tailings is dependent on its co-precipitation with barium, lead or calcium sulfate. It is imperative therefore that the relationship between the solubility of Ra-226 and such co-precipitation be well understood.

To achieve these objectives, a series of metal sulfates (M=Pb,Ba,Ca) have been prepared and doped with varying concentrations of Ra-226. Solubility studies of these labelled salts have been carried out as a function of pH, sulfate concentration and ferrous iron concentration in order to measure the release of Ra-226 from the host matrix. The concentration levels selected for Ra-226 were chosen so that the anticipated release of Ra-226 would be in the range of 0.5 - 50 Bq/l, levels that cover the range of Ra-226 activity observed in uranium mill tailings porewaters. In addition the lead sulfate salt was labelled with the radiotracer Pb-210 and the barium sulfate salt was labelled with the radiotracer Ba-133. It is easier to detect low concentrations of radiotracers by nuclear analytical techniques than it is to detect stable isotopes by conventional analytical methods; hence, the inclusion of the radiotracers was considered desirable to improve the overall data quality.

The oxidation of pyrite in uranium mill tailings leads to lower pH values and higher ferrous iron and sulfate concentrations which can alter the solubility of Ra-226. When these solutions are made neutral, i.e., pH 6-8, under oxidative conditions, Fe(II) is precipitated as ferric hydrous oxide which can remove trace cations with it. The latter situation is applicable to porewater existing in uranium mill tailings, be it to surface or to ground water. Accordingly it is desirable to obtain information on the effectiveness of and mechanism by which ferric hydrous oxide can remove Ra-226. Such information would provide a better understanding of the converse reaction, that is, the release of Ra-226 from ferric hydrous oxide.

Accordingly experiments were designed to determine whether or not Ra-226 will coprecipitate with ferric hydrous oxide and if so, the degree of efficiency of coprecipitation from saturated sulfate salt solutions containing Ra-226. Further tests were conducted to analyze the ferric hydrous oxide precipitates by the method of selective sequential extractions to assess the tenacity with which the co-precipitated Ra-226, if any, is held by the host matrix.

2. Experimental

2.1. Preparation of Ra-226 Labelled Sulfate Salts of Calcium, Lead and Barium.

Samples of each metal sulfate were prepared and labelled with different activity levels of Ra-226, denoted high, intermediate and low. The levels of activity chosen were calculated so that a saturated solution of the host salt would yield radium activities in solution varying from approximately 0.5 to 50 Bq/l provided that Ra-226 dissolves in proportion to the host matrix. This range is considered typical for both surface runoff and uranium tailings porewaters. In addition, the lead sulfate salt was also labelled with Pb-210 and the barium sulfate salt was labelled with Ba-133.

2.1.1. Preparation of Ra-226 Labelled Calcium Sulfate

The nominal radium-226 activities selected to be prepared were as follows:

High	-	20 Bq Ra-226/gm calcium sulfate
Intermediate	-	2 Bq Ra-226/gm calcium sulfate
Low	-	0.2 Bq Ra-226/gm calcium sulfate

Twenty grams of each of the high and low Ra-226 labelled salts were to be prepared; one hundred grams of the intermediate Ra-226 labelled salt were also to be prepared. In all cases, the calcium sulfate salts were precipitated from equimolar mixtures of calcium chloride and sodium sulfate in pH 3 sulfuric acid. The carrier-free radium-226 activity was added to the calcium chloride prior to addition to the sodium sulfate solution. The Ra-226 labelled calcium sulfate was then collected in a Buchner funnel, washed with deionized water and oven dried at 190 Deg. C. Samples were stored in capped glass bottles.

2.1.2. Preparation of Ra-226 Labelled Lead Sulfate

The nominal radium-226 activities selected were as follows:

High	-	1200 Bq Ra-226/gm lead sulfate
Intermediate	-	120 Bq Ra-226/gm lead sulfate
Low	-	12 Bq Ra-226/gm lead sulfate

In addition each salt was labelled with 3.7 kBq Pb-210/gm lead sulfate. Twenty grams of each of the high and low Ra-226 labelled salts were prepared; fifty grams of the intermediate Ra-226 labelled salt were also prepared. In all cases the lead sulfate salts were precipitated from equimolar mixtures of lead nitrate and potassium sulfate. The Ra-226 labelling was carried out as described in Sec 2.1.1. and the labelled lead sulfate was collected and dried at 105 Deg. C.

2.1.3. Preparation of Ra-226 Labelled Barium Sulfate

The radium-226 activities selected were as follows:

High	-	20 kBq Ra-226/gm barium sulfate
Intermediate	-	2 kBq Ra-226/gm barium sulfate
Low	-	0.2 kBq Ra-226/gm barium sulfate

In addition each salt was labelled with 74 kBq Ba-133/gm barium sulfate. The amounts of high, intermediate and low Ra-226 labelled salts prepared were as described in Sec. 2.1.2. In all cases the barium sulfate salts were prepared by precipitation from equimolar solutions of barium chloride and potassium sulfate. The precipitated salts were collected, dried and stored as described above.

2.2. Analysis of Ra-226 Labelled Sulfate Salts of Calcium, Lead and Barium

Each of the metal salts was analyzed for metal content, Ra-226 activity and tracer activity, if applicable. Replicate subsamples were analyzed to ensure sample homogeneity.

The major cations of calcium, lead and barium were analyzed by classical wet methods as follows:

Calcium - Subsamples of calcium sulfate (0.500 gm) were dissolved in concentrated hydrochloric acid and diluted to 100 mls. Aliquots of this solution were then titrated with standard EDTA solution using Eriochrome Black T as indicator.

Lead - Subsamples of lead sulfate (0.300 gm) were dissolved in ammonium acetate and then aliquots titrated with EDTA using tannic acid as an external indicator.

Barium - Subsamples of barium sulfate (0.500 gm) were fused with sodium carbonate and leached with water to remove sulfate. The barium carbonate was then dissolved with hydrochloric acid and aliquots taken to determine barium gravimetrically as barium sulfate.

Radium-226 - Ra-226 was determined by alpha counting techniques following a radiochemical separation, purification and coprecipitation with barium sulfate. Ba-133 was used as a tracer to monitor the overall yield of the radium separation.

Lead-210 - Pb-210 was determined by gamma spectroscopy using its 46.5 KeV gamma ray.

Barium-133 - Ba-133 was determined by gamma spectroscopy using its 356 KeV gamma ray.

Results of the characterization of the Ra-226 labelled sulfate salts are presented in Table 1.

2.3. Studies to determine Time Required for Equilibration

In order to determine the time required for equilibrium to be attained in the solubility studies, samples of each of calcium sulfate, lead sulfate and barium sulfate were shaken in a solution of pH 4 and the concentration of the major cation was followed as a function of time. All metal sulfates containing the intermediate Ra-226 activity were used and a solid: liquid ratio of 1:100 was maintained. Calcium was determined by EDTA titration as described in Sec.2.2. Lead and barium were determined by flame atomic absorption spectroscopy. Analytical results are presented in Table 2.

2.4. Solubility of Labelled Metal Sulfates as a Function of pH

The metal sulfate salts containing the intermediate level of Ra-226 activity were tested to measure their solubility as a function of pH in the range 1-8; in addition, the metal sulfate salts containing both high and low levels of Ra-226 activity were tested at pH 4 to measure their solubility. Solutions of pH, 1, 1.5 (Ca only), 2, 3, 4, 5, 6, 7, 8 were prepared by adjusting deionized water with a minimum amount of dilute nitric acid or sodium hydroxide solution. A pH of 1.5 was used for calcium sulfate only because of its complete solubility at pH 1 for the solid:liquid ratio of 1:100 (10 gms/1) used in all these tests. The pH of each solution was checked after addition of the metal sulfate and again at the end of equilibration to ensure that no significant change had occurred. Samples were shaken for 24 hours, a time demonstrated (see Table 2) to be sufficient for equilibrium to be attained. At that time, samples were filtered through 0.45 u cellulose acetate and acidified with nitric acid (2 mls conc. acid/1). The undissolved material was washed thoroughly with deionized water and dried for re-use according to its original method of preparation. The preserved filtrate was analyzed for the major cation (Ca) or radiotracer (Pb-210, Ba-133) and Ra-226 as described in Sec. 2-2. For the metal sulfates of intermediate Ra-226 activity, test results are tabulated in Table 3-1 (calcium sulfate), Table 3-2 (lead sulfate) and Table 3-3 (barium sulfate). For the metal sulfates of high and low Ra-226 activity, test results are tabulated in Table 3-4.

2.5. Solubility of Labelled Metal Sulfates as a Function of Sulfate Concentration

The metal sulfate salts containing the intermediate level of Ra-226 activity were tested to measure their solubility as a function of sulfate concentration at pH 4. The sulfate - containing solutions were prepared from potassium sulfate and had sulfate concentrations of 500, 2000, 5000, 10000 and 15000 mg/1 SO4. The solubility of each metal sulfate salt was tested using a solid:liquid ratio of 1:100 (typically 10 gms per litre of sulfate solution). Time allowed for equilibration was 24 hrs. of shaking and then solutions were filtered, preserved and analyzed as described in Sec. 2.4. Results of these experiments are presented in Table 4.

2.6. Solubility of Labelled Metal Sulfates as a Function of Ferrous Iron Concentration at pH 3.5

The metal sulfate salts containing the intermediate level of Ra-226 activity were tested to measure their solubility as a function of ferrous iron concentration at pH 3.5. The ferrous iron solutions were prepared from ferrous sulfate heptahydrate, stabilized with 0.5% w/v ascorbic acid, and had concentrations of 100, 500, 1000, 5000 and 10000 mg/l Fe(II). The solubility of each metal sulfate salt was tested using a solid:liquid ratio of 1:100. The test solutions were purged of oxygen by sparging with nitrogen gas prior to shaking for 24 hours to allow equilibrium to be attained. The solutions were then filtered, preserved and analyzed as described in Sec. 2-4. Results of these experiments are presented in Table 5.

2.7. Precipitation of Ferric Hydrous Oxide

The experiments described in Sec. 2.6. were repeated and the preserved solutions were oxidized with 15.0 mls of 30% w/v hydrogen peroxide at 70 Deg.. C for three hours to oxidize ferrous iron. The solution was then boiled to expel excess hydrogen peroxide and the solution neutralized with sodium carbonate to precipitate ferric hydrous oxide. The precipitate was collected on a tared Whatman GF/F filter paper, dried at 105 Deg. C, cooled in a desiccator and weighed. The masses of the ferric hydrous oxide precipitates are tabulated in Table 6.

2.8. Sequential Extraction of Ferric Hydrous Oxide Samples

The ferric hydrous oxide samples obtained in Sec. 2.7. were subjected to sequential extraction according to the method of Tessier et al. (6) in order to determine the availability of any co-precipitated Ra-226.

(i) Exchangeable Ra-226: Ferric hydrous oxide samples were extracted at room temperature for 1 hr by continuous agitation with 10 mls of 1M magnesium chloride solution, pH 7.0. The extracts were analyzed for Ra-226 and the insoluble residue further extracted as described below.

(ii) Ra-226 Bound to Carbonates: The insoluble residue from (i) was leached at room temperature with 8 mls of 1M sodium acetate adjusted to pH 5.0 with acetic acid. Continuous agitation was maintained for at least 5 hrs to ensure complete extraction. The extracts were analyzed for Ra-226 and the insoluble residue further extracted as described below.

(iii) Ra-226 Bound to Fe-Mn oxides: The insoluble residue from (ii) was extracted with 20 mls of 0.04M hydroxylamine hydrochloride in 25% (v/v) acetic acid at 96 +/- 3 Deg. C for at least 6 hrs to ensure complete extraction. The extracts were analyzed for Ra-226 and the insoluble residue further analyzed as described below.

(iv) Residual Ra-226: The insoluble residue from part (iii)

was then dissolved entirely by digestion with a mixture of hot concentrated hydrofluoric, nitric and perchloric acids. The digest solution was then analyzed for Ra-226. Residual Ra-226 was determined for residues derived from calcium sulfate and lead sulfate but not barium sulfate.

For the ferric hydrous oxide samples obtained from the two highest ferrous iron concentrations, the sequential extraction was performed using 2.00 gm subsamples. The data however have been calculated on the mass of the entire precipitate.

The results of this series of experiments are presented in Table 7.

TABLE 1

Analysis of Ra-226 Labelled Sulfate Salts of Calcium, Lead and Barium

A. Ca (Ra-226) SO4

	Bq Ra-226/gm	% Ca
High Ra-226	4.16	29.7
High Ra-226	4.01	29.3
High Ra-226	4.31	29.6
Intermediate Ra-226	1.02	28.9
Intermediate Ra-226	1.00	29.4
Intermediate Ra-226	0.92	29.3
Low Ra-226	0.29	29.8
Low Ra-226	0.28	29.3
Low Ra-226	0.26	29.7
	Theoretical:	29.4

B. Pb (Ra-226, Pb-210) SO4

	Bq Ra-226/gm	% Pb	kBq Pb-210/gm
High Ra-226	1180	69.4	3.78
High Ra-226	1250	69.4	3.70
High Ra-226	1100	69.3	3.74
Intermediate Ra-226	116	69.5	3.58
Intermediate Ra-226	116	69.5	3.76
Intermediate Ra-226	118	69.7	3.76
Low Ra-226	14.9	69.6	3.63
Low Ra-226	13.3	69.3	3.77
Low Ra-226	14.0	69.7	3.70
	Theoretical:	68.3	

C. Ba (Ra-226, Ba-133) SO4

	kBq Ra-226/gm	% Ba	kBq Ba-133/gm
High Ra-26	20.9	58.0	75.0
High Ra-226	21.4	57.9	74.4
High Ra-226	21.3	--	74.6
Intermediate Ra-226	1.95	58.0	73.0
Intermediate Ra-226	1.85	57.9	72.6
Intermediate Ra-226	1.75	--	73.9
Low Ra-226	0.194	57.9	73.7
Low Ra-226	0.194	57.8	73.6
Low Ra-226	0.174	--	73.5
	Theoretical:	58.8	

TABLE 2

Concentrations of Metal Sulfates During Equilibration at pH 4

Time (hrs)	[CaSO4] mg/l	[PbSO4] mg/l	[BaSO4] mg/l
1	2145	38	7.0
2	2050	38	3.9
4	2220	37	3.1
16	2160	--	--
24	2060	39	1.7
72	2070	--	1.7

TABLE 3-1

Solubility of Ca(Ra-226)SO4 for the Intermediate Ra-226 Activity as a Function of pH

pH	[CaSO4] mg/l	[Ra-226] Bq/l
1.5	8055	9.70
2	3385	9.40
3	2140	8.79
4	2060	8.81
5	2080	9.48
6	2040	9.47
7	2055	8.09
8	2070	9.14

TABLE 3-2

Solubility of Pb(Pb-210, Ra-226)SO4 for the Intermediate Ra-226 Activity as a Function of pH

pH	[Pb-210] Bq/l	[PbSO4]* mg/l	[Ra-226] Bq/l
1	1660	449	3.22
2	308	83	1.44
3	197	53	1.18
4	141	39	0.89
5	126	34	0.89
6	116	31	1.41
7	156	42	0.52
8	179	49	1.18

* calculated from Pb-210/Pb ratio of 3.70 kBq/gm PbSO4

TABLE 3-3

Solubility of Ba(Ba-133,Ra-226)SO4 for the Intermediate Ra-226 Activity as a Function of pH

pH	[Ba-133] Bq/l	[BaSO4]* mg/l	[Ra-226] Bq/l
1	4330	58.5	111
2	191	2.6	2.89
3	79	1.1	1.15
4	99	1.3	1.15
5	127	1.7	1.33
6	98	1.3	1.41
7	120	1.6	1.96
8	91	1.2	1.85

* calculated from Ba-133/Ba ratio of 74 kBq Ba-133/gm BaSO4

TABLE 3-4

Solubility of Metal Sulfates Containing High, Intermediate and Low Activities of Ra-226 at pH4

A. Calcium Sulfate

Ra-226 Activity Level	[CaSO4] mg/l	[Ra-226] Bq/l
High	2035	25.5
Intermediate	2060	8.81
Low	2035	2.78

B. Lead Sulfate

Ra-226 Activity Level	[Pb-210] Bq/l	[PbSO4] mg/l	[Ra-226] Bq/l
High	144	39	4.96
Intermediate	141	39	0.89
Low	136	37	0.24

C. Barium Sulfate

Ra-226 Activity Level	[Ba-133] Bq/l	[BaSO4] mg/l	[Ra-226] Bq/l
High	74	1.0	9.00
Intermediate	99	1.3	1.15
Low	119	1.6	0.15

TABLE 4

Solubility of Metal Sulfate Salts Containing Intermediate Ra-226 Activity Levels as a Function of Sulfate Concentration at pH4.

A. Calcium Sulfate

[SO4] mg/l	[CaSO4] mg/l	[Ra-226] Bq/l
0	2060	8.81
500	1835	9.19
2000	1560	8.84
5000	1390	7.85
10000	1410	7.47
15000	1450	8.30

B. Lead Sulfate

[SO4] mg/l	[Pb-210] Bq/l	[PbSO4] mg/l	[Ra-226] Bq/l
0	141	39	0.89
500	17.8	4.8	0.37
2000	14.1	3.8	0.63
5000	10.7	2.9	6.48
10000	4.4	1.2	1.00
15000	2.6	0.7	0.48

C. Barium Sulfate

[SO4] mg/l	[Ba-133] Bq/l	[BaSO4] mg/l	[Ra-226] Bq/l
0	99	1.3	1.15
500	10	0.1	0.08
2000	5	<0.1	0.10
5000	30	0.4	0.13
10000	<5	<0.1	0.04
15000	5	<0.1	0.10

TABLE 5

Solubility of Metal Sulfate Salts Containing Intermediate Ra-226 Activity Levels as a Function of Ferrous Iron Concentration at pH 3.5

A. Calcium Sulfate

[FeII] mg/l	[CaSO4] mg/l	[Ra-226] Bq/l
100	2095	8.73
500	2040	9.80
1000	1890	9.24
5000	1685	9.12
10000	1715	9.30

B. Lead Sulfate

[FeII] mg/l	[Pb-210] Bq/l	[PbSO4] mg/l	[Ra-226] Bq/l
100	17.4	4.7	1.26
500	15.2	4.1	1.85
1000	15.2	4.1	1.30
5000	13.7	3.7	0.52
10000	14.1	3.8	0.30

C. Barium Sulfate

[FeII] mg/l	[Ba-133] Bq/l	[BaSO4] mg/l	[Ra-226] Bq/l
100	40	0.6	0.19
500	10	0.1	0.10
1000	10	0.1	0.07
5000	15	0.2	0.14
10000	40	0.6	0.11

TABLE 6

Mass (gm) of Ferric Hydrous Oxide Precipitates

Original Ferrous Iron Concentration mg/l	from calcium sulfate (g/l)	from lead sulfate (g/l)	from barium sulfate (g/l)
100	2.379	0.072	0.003
500	2.502	0.018	0.214
1000	2.958	2.350	2.234
5000	10.878	9.120	10.060
10000	19.66	19.464	19.364

TABLE 7

Sequential Extraction of Ferric Hydrous Oxide for Radium-226

A. Calcium Sulfate

Original Fe(II) Conc. (mg/l)	Ra-226 (Bq) Exchangeable	Bound to Carbonate	Bound to Fe-Mn Oxides	Residual	Sum	% of Total
100	0.12	0.12	0.20	1.34	1.78	30
500	0.07	0.10	0.13	3.23	3.53	36
1000	0.04	0.31	1.02	2.84	4.21	46
5000	0.29	0.46	0.99	4.83	6.57	72
10000	0.10	0.24	0.62	6.19	7.15	77

B. Lead Sulfate

Original Fe(II) Conc. (mg/l)	Ra-226 (Bq) Exchangeable	Bound to Carbonate	Bound to Fe-Mn oxides	Residual	Sum	% of Total
100	0.02	0.03	0.07	0.01	0.13	10
500	0.02	0.01	<0.01	<0.01	0.03	2
1000	0.03	0.01	0.01	<0.01	0.05	4
5000	0.08	<0.01	0.29	0.03	0.40	71
10000	0.32	<0.01	0.07	0.02	0.41	100

C. Barium Sulfate

Original Fe(II) Conc. (mg/l)	Ra-226 (Bq) Exchangeable	Bound to Carbonate	Bound to Fe-Mn oxides	Sum	% of Total
100	0.03	<0.01	<0.01	0.03	16
500	<0.01	<0.01	<0.01	<0.01	0
1000	<0.01	<0.01	<0.01	<0.01	0
5000	<0.01	<0.01	<0.01	<0.02	0
10000	<0.02	<0.01	0.04	0.04	36

3. Results and Discussion

Calcium sulfate proved to be rather reluctant to accept Ra-226 into its crystal matrix. As a result, the Ra-226 activity within the calcium sulfate was somewhat different (Table 1) than the design values. It was demonstrated that only 2-3% of the Ra-226 would coprecipitate with calcium sulfate under the test conditions used, no doubt due to the disparity in the atomic radii of the cations which prevents Ra-226 from fitting easily into the lattice. It is well known, on the other hand, that both lead sulfate and barium sulfate are extremely effective in co-precipitating radium-226 and the analytical data (Table 1) show that Ra-226 was coprecipitated quantitatively and homogeneously.

A period of 24 hours was used in the shaking tests as the data (Table 2) show that equilibrium is attained in this period of time. The solubility of barium sulfate was observed to decrease during this 24 hr. period, a behaviour noted by other experimenters (1) and generally attributed to supersaturation due to microcrystals. The ageing of the precipitate permits a slow digestion towards a larger crystal size and an equilibrium solubility. In the equilibrium study, concentrations of both barium and lead were determined by atomic absorption spectroscopy, thus permitting a comparison with data generated by radiochemical methods (Table 3-4).

The variation of the solubility of Ca(Ra)SO4 with respect to pH is presented in Table 3-1 and graphically in Figure 1. The solubility measured at pH 7 (2055 mg/l) is in excellent agreement with recently published data of 2090 mg/l (2). The solubility of calcium sulphate does not vary significantly in the pH range from 4 to 8. At lower pH values, the solubility increases dramatically. The lowest pH value tested was 1.5 since a pH of 1 was found to completely dissolve the salt using a solid:liquid ratio of 1:100. The release of Ra-226 from the calcium sulfate is consistently high and uniform, regardless of pH (Fig. 1). Since the Ra-226 content of the calcium sulfate is 0.98 Ba/gm, the maximum Ra-226 release possible is 9.8 Bq/l. Over the entire pH range, the release of Ra-226 is approximately 90% of this total.

The variation of the solubility of Pb(Ra)SO4 with respect to pH is presented in Table 3-2 and graphically in Figure 2. The solubility measured at pH 7 (42 mg/l) is in excellent agreement with recently published data of 42.5 mg/l (2) and 42.3 mg/l (3). The solubility of lead sulfate shows a minimum at pH 5 and 6 and increases towards both higher and lower pH values. It is significant to note that Ra-226, although present in the salt with an activity of 117 Bq/gm, is preferentially retained in the solid phase and does not dissolve in proportion to the host matrix. For example, at pH 5 the dissolution of 34 mgs of lead sulfate might be expected to release 3.98 Bq of Ra-226 and yet only 0.89 Bq are observed. At lower pH values, the percentage of Ra-226 observed versus what might be expected in proportion to the solubility of lead declines steadily from 22% to only 5.6% at pH 1. Evidently Ra-226 is thermodynamically more stable when present within the lead sulfate crystal.

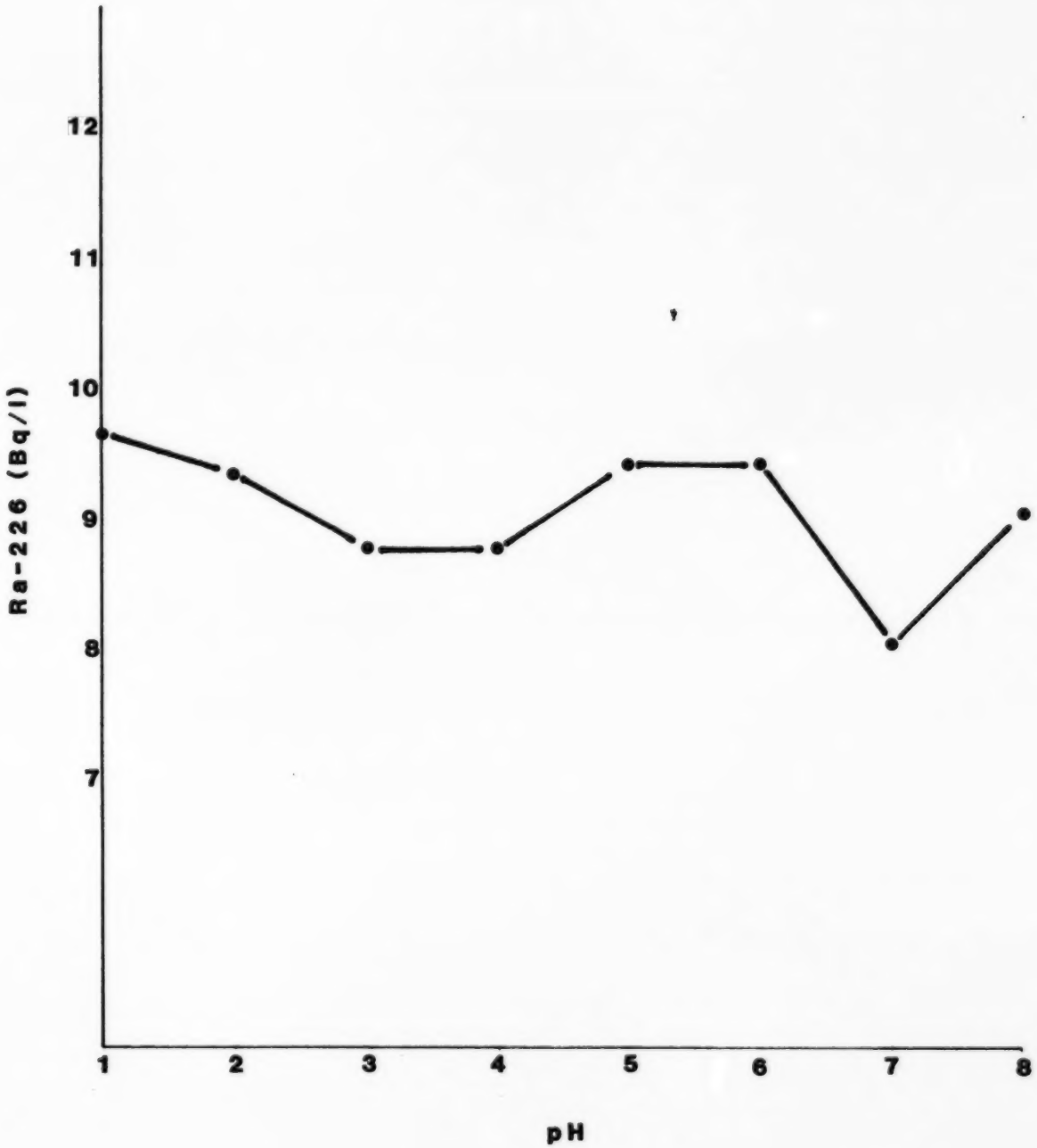

Figure 1: Release of Ra-226 from calcium sulfate as a function of pH

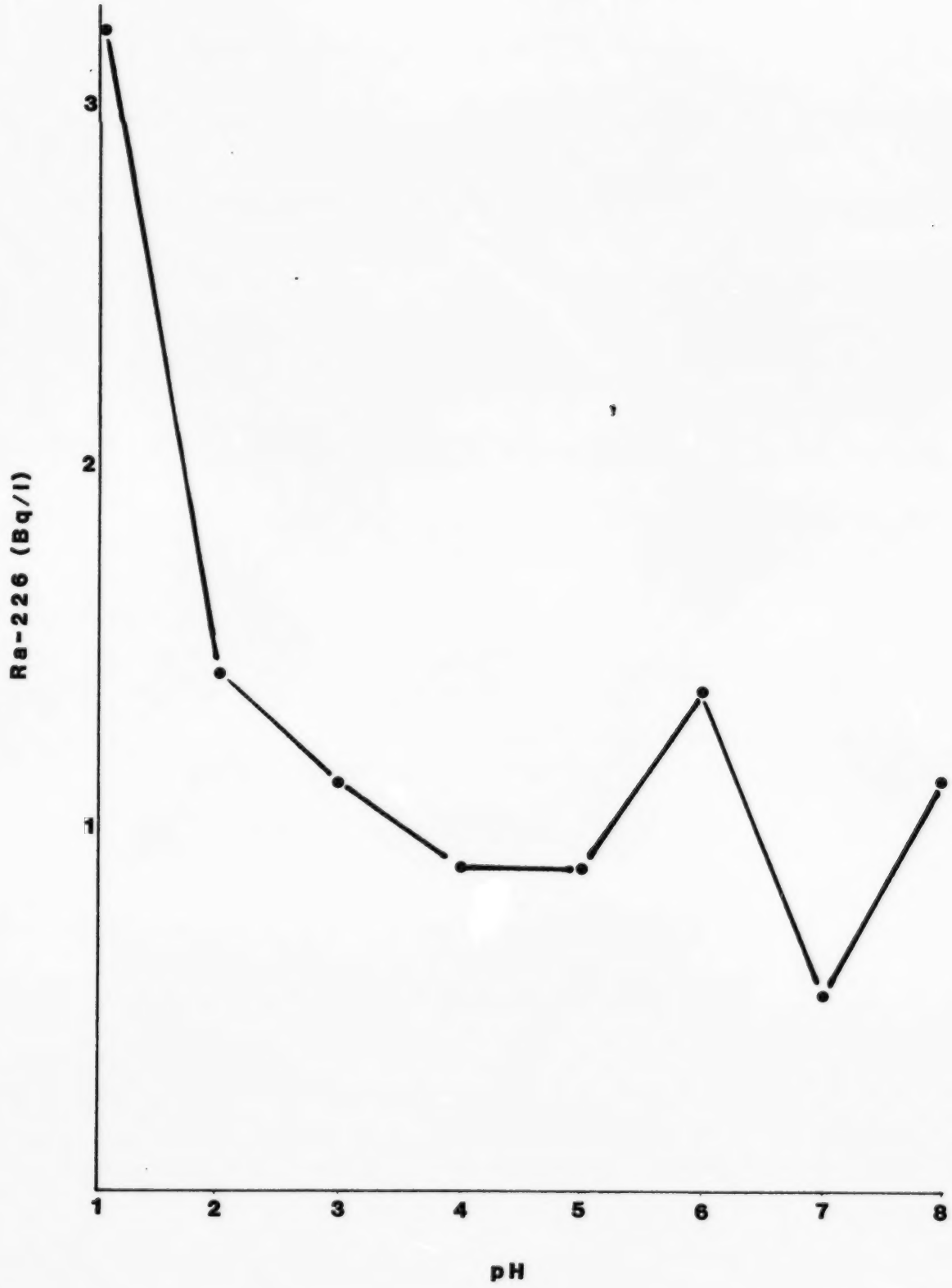

Figure 2: Release of Ra-226 from lead sulfate as a function of pH

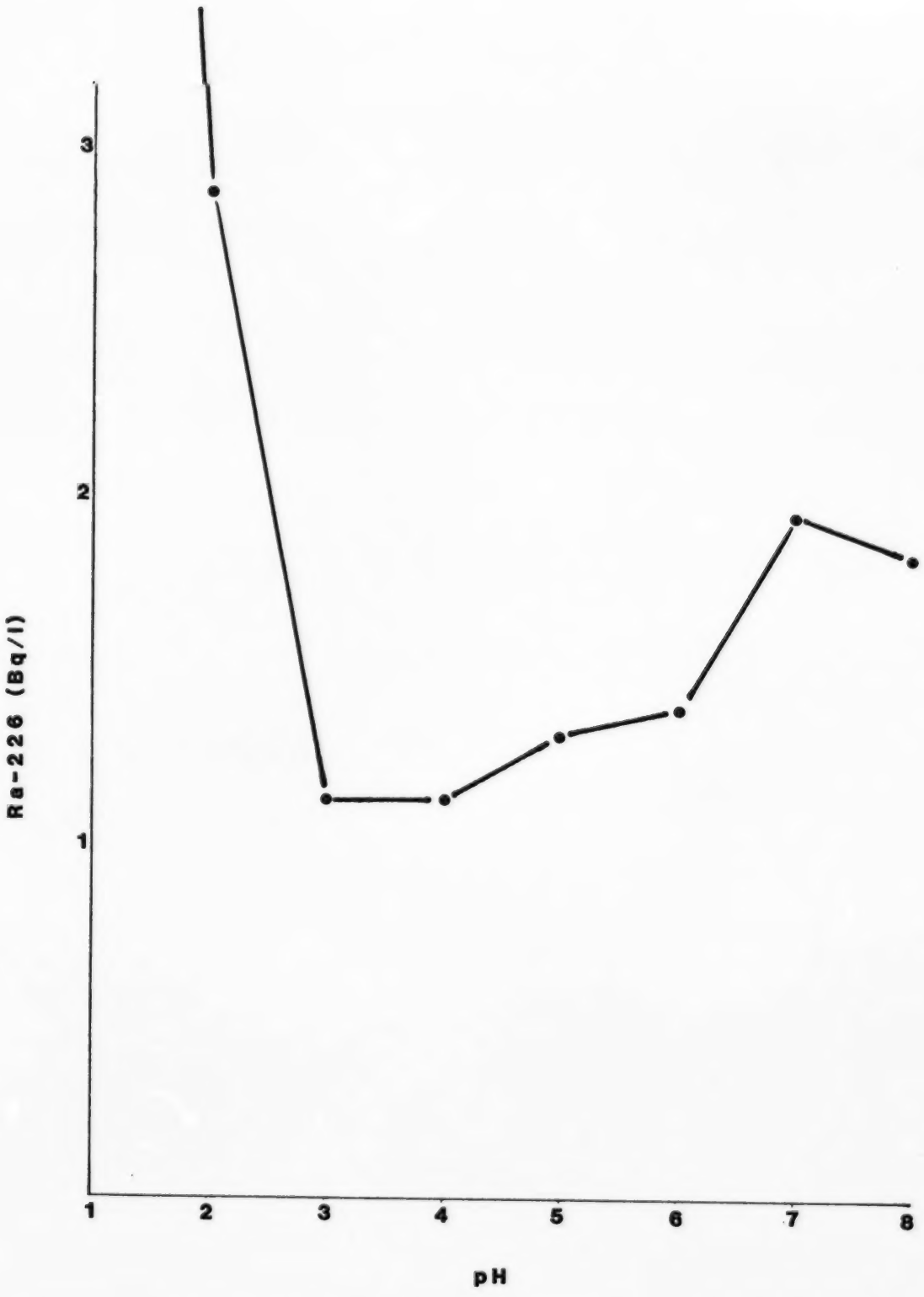

Figure 3: Release of Ra-226 from barium sulfate as a function of pH

The variation of the solubility of Ba(Ra)SO4 with respect to pH is presented in Table 3-3 and graphically in Figure 3. The solubility measured at pH 7 (1.6 mg/l) is somewhat less than that of published data of 2.2 mg/l (2). As noted earlier however, there is good agreement between data obtained by atomic absorption spectroscopy (Table 2) and gamma spectroscopy (Table 3-4). Perhaps the ageing of the precipitate in a factor as it has been noted previously (4) that Ba-133 and Ra-226 release from labelled barium sulfate decreases with time. The solubility of the barium sulfate shows little variability in the pH range of 3-8. The release of Ra-226 is a minimum at pH 3,4 and increases smoothly towards higher and lower pH values. At pH 1, significant quantities of Ra-226 are released (111 Bq/l) and it can be calculated that the Ra-226 is being released in directed proportion to the solubility of the host matrix (58.5 mgs of BaSO4 contain 108 Bq of Ra-226). At more neutral pH values of 3-6, the amount of Ra-226 that dissolves is about one half of what one might expect if it dissolves in direct proportion to its activity in the host matrix. At pH values of 7-8, about three quarters of the Ra-226 dissolves. It appears once again that Ra-226 is preferentially retained in the precipitate but the degree is not nearly as pronounced as in PbSO4 and indeed is directly opposite at the lowest pH measurements.

The differences between the two salts is illustrated again in Table 3-4. The results of the experiments with three different activity levels of Ra-226 show that, in barium sulfate, a ten-fold increase of Ra-226 activity in the salt is reflected by a ten-fold increase of Ra-226 in solution; by contrast, a ten-fold increase of Ra-226 activity in lead sulfate is reflected by only a five-fold increase of Ra-226 in solution. The solubilities of the host matrices are essentially unaffected by the varying activities of Ra-226. Results of the study with calcium sulfate show that Ra-226 is released quantitatively from the salt with the low Ra-226 activity level, approximately 90% from the intermediate activity level and approximately 65% from the high activity level.

Table 4 illustrates the solubility of the metal sulfate salts as a function of the relatively high sulfate concentrations that can be found in uranium tailings porewaters. The solubility of calcium sulfate decreases with increasing sulfate concentration but the decrease is not very large, no doubt because there are significant sulfate concentrations present from the salt alone due to its solubility. The release of Ra-226 is substantial and largely independent of the sulfate concentration, although there is some evidence of a slight reduction of Ra-226 activity for the higher sulfate concentrations.

The solubility of the lead sulfate is observed to decrease steadily with increasing sulfate concentration. The behaviour of Ra-226 on the other hand is quite dissimilar; the solubility of Ra-226 is actually enhanced by both 5000 and 10,000 ppm sulfate. The solubility at 5000 ppm sulfate is particularly perplexing; the experiment was actually repeated in triplicate with fresh solutions and freshly labelled salts but the results were unchanged. It is not clear why the solubility of Ra-226 should increase so significantly. Most likely the high potassium concentration in the potassium sulfate

solution results in partial displacement of Ra-226 from the lead sulfate. Previous authors (5) have noted the effect of cations on Ra-226 solubility and consider that the effectiveness of cation exchange depends not only on the concentration of the cation solution, but also on its valence, ionic radius, atomic weight, and the redox behaviour of the medium.

The solubility of barium sulfate as a function of sulfate was not particularly informative since the solubility was depressed to the limit of quantitation. In contrast to its behaviour in lead sulfate, the Ra-226 activity levels decrease significantly to very low levels without any particularly distinctive features.

Table 5 tabulates the solubility of the labelled metal sulfate salts as a function of ferrous iron concentration. The ferrous iron solutions were prepared from ferrous sulfate heptahydrate so that it is important to note that considerable sulfate concentrations are also present. A series of figures has been prepared to illustrate the pattern of Ra-226 release from the various metal salts as a function of both potassium sulfate and ferrous sulfate solutions. The relevant figures are Fig. 4 (calcium sulfate), Fig. 5 (lead sulfate) and Fig. 6 (barium sulfate).

The solubility of calcium sulfate is observed to decrease fractionally with increasing ferrous sulfate concentration. The decrease is significantly less than observed in the potassium sulfate system. The release of Ra-226 is consistently high, almost quantitative, and independent of ferrous sulfate concentration.

The solubility of lead sulfate at the lowest ferrous iron concentrations is very similar to that observed at the two lowest sulfate concentrations (Table 4); however, the solubility does not change significantly at the higher ferrous iron concentrations of 5000 and 10,000 ppm Fe, despite the higher associated sulfate concentrations. This behaviour is distinctly different from that exhibited by lead sulfate in the presence of potassium sulfate (Table 4). The solubility of Ra-226 is also different in the ferrous sulfate aqueous system; at the three lowest ferrous iron concentrations, the solubility of Ra-226 is enhanced and shows a general decrease in solubility with increasing ferrous iron concentration.

The solubility of barium sulfate as a function of ferrous sulfate concentration was not particularly informative. The solubility was severely depressed as noted previously for the potassium sulfate solutions; it does appear that the solubility is fractionally higher than for the potassium sulfate solutions. The release of Ra-226 is also significantly depressed and the Ra-226 activity levels are similar to those exhibited in potassium sulfate solutions (Table 4).

The ferrous sulfate solutions containing saturated amounts of the various metal sulfates and associated Ra-226 were then oxidized and neutralized to precipitate ferric hydrous oxide. The masses of the ferric hydrous oxide precipitates are recorded in Table 6. It is apparent in the calcium sulfate system that neutralization with sodium carbonate causes precipitation of calcium carbonate along with ferric

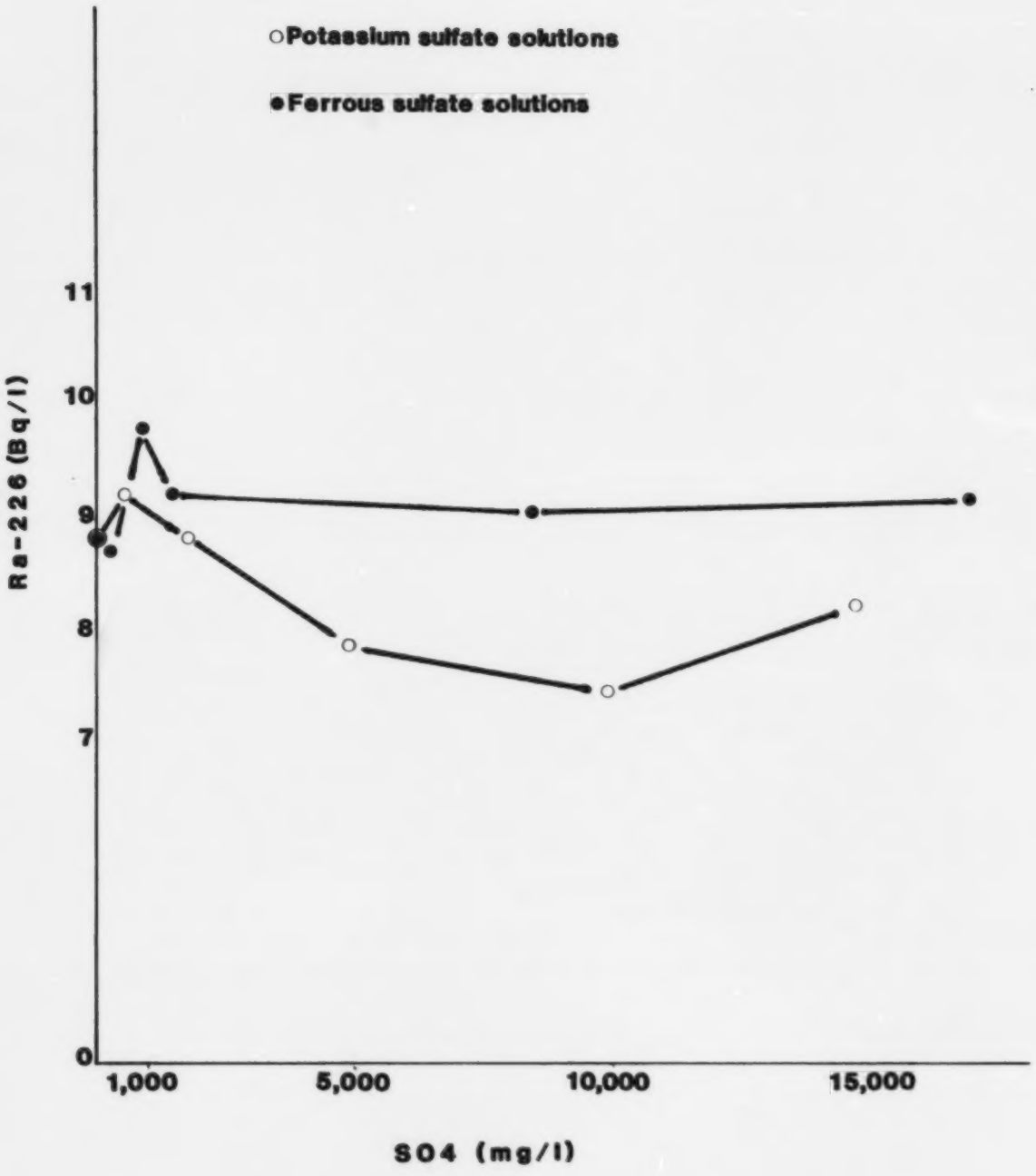

Figure 4: Release of Ra-226 from calcium sulfate as a function of sulfate concentration

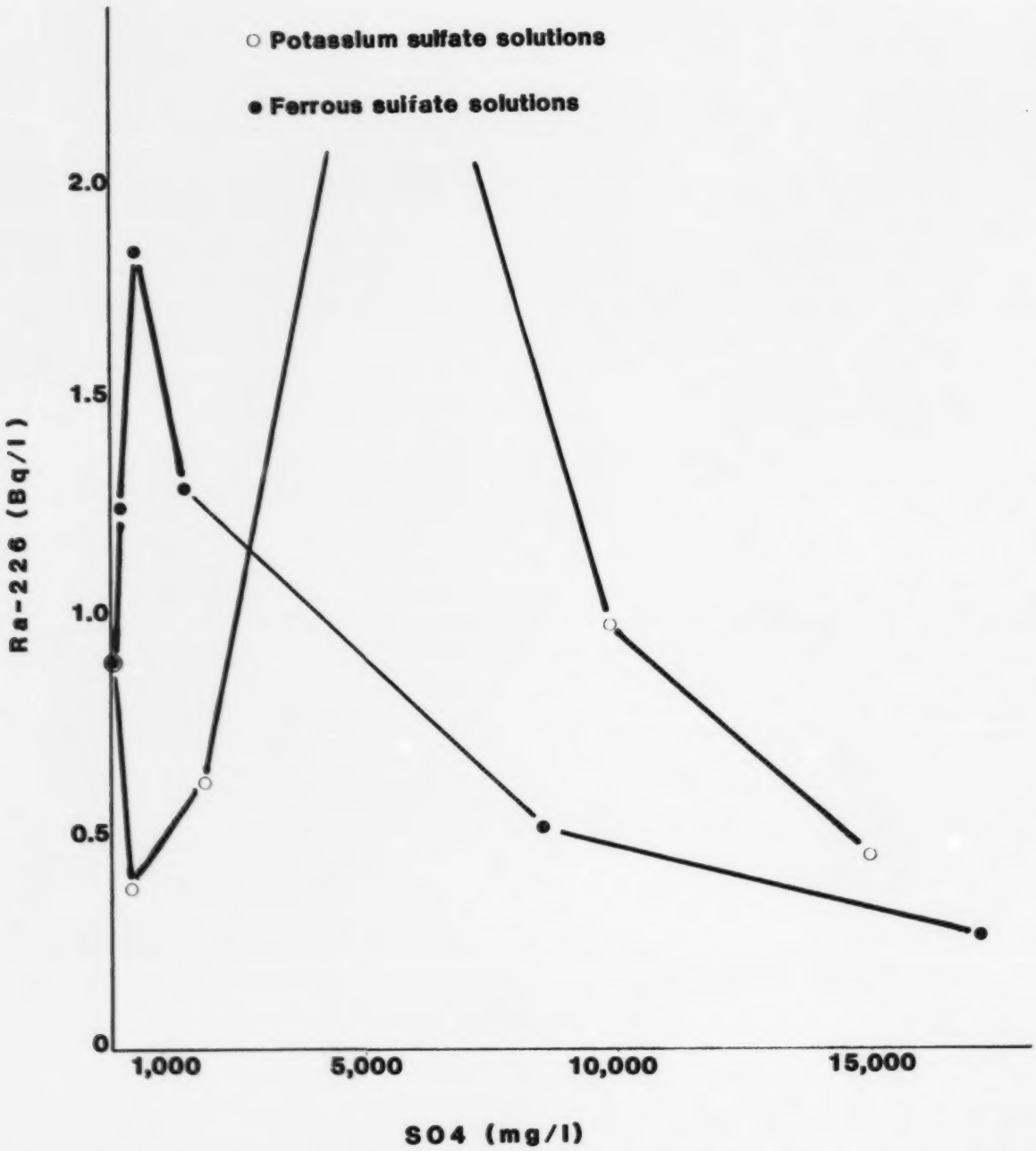

Figure 5: Release of Ra-226 from lead sulfate as a function of sulfate concentration

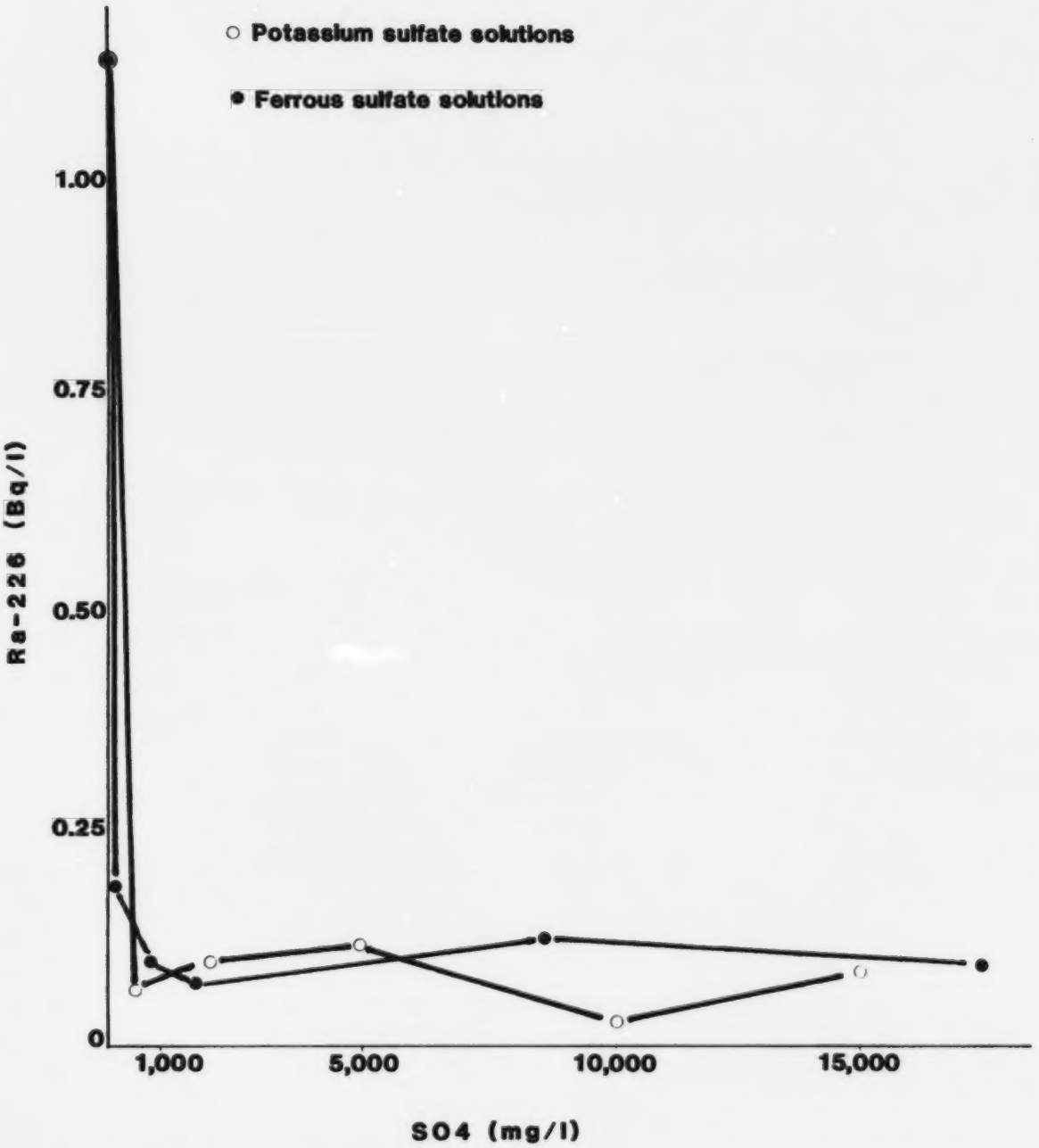

Figure 6: Release of Ra-226 from barium sulfate as a function of sulfate concentration

hydrous oxide. Precipitates from the lowest ferrous iron solutions ranged in colour from white (100 mg/l Fe) to tan (1000 mg/l). The highest iron solutions exhibited the typical brick red-brown colour of ferric iron. The masses of the precipitates are also consistent with the formation of calcium carbonate given the initial solubility of calcium sulfate. Although barium carbonate is even more insoluble, the very much lower solubility of barium sulfate means that the amount of soluble barium available for precipitation is not significant. The precipitation of ferric hydrous oxide is not necessarily expected to be quantitative, yet a comparison of precipitate masses from the 1000, 5000 and 10000 mg/l ferrous iron solution show a very consistent pattern of increase. For the two highest ferrous iron solutions, only a portion (2.00 gm) was treated to the sequential extraction so as to handle manageable quantities. The sequential extraction data are summarized in Table 7.

The most informative set of experiments was the sequential extraction of ferric hydrous oxide obtained from the calcium sulfate solutions. The calcium sulfate solutions had significant quantities of Ra-226 in solution and thus it was possible to follow that fate of Ra-226 with good statistical certainty. The data show that ferric hydrous oxide is quite capable of coprecipitating Ra-226, even at the lowest original concentration of ferrous iron. It is also clear that the greater the mass of precipitating ferric hydrous oxide, the greater the quantity of Ra-226 this is coprecipitated. In each of the sequential extractions, detectable Ra-226 was found for all concentrations of the original ferrous iron. Most of the Ra-226 was found in the residual fraction although this may be an artifact of the sequential extraction procedure. The procedure is really designed for soils and lake or river sediments; the proportion of reagents is therefore most appropriate to samples of this type and not to a sample completely consisting of ferric hydrous oxide. It is likely that a greater proportion of the Ra-226 would be amenable to the hydroxylamine hydrochloride leach (Bound to Fe-Mn oxides) if saturation was not achieved because of the relatively low solid:liquid ratio.

Precipitation of the lead sulfate solutions was found to bring down at least traces of Ra-226 in all cases; at the two highest ferrous iron concentrations, the greater mass of precipitated ferric hydrous oxide was more effective in co-precipitating Ra-226. Within experimental uncertainty relating to the counting statistics, Ra-226 is precipitated quantitatively from the 10,000 ppm ferrous solution.

Analysis of the precipitates from the barium sulfate solutions was more problematic in that the Ra-226 present in solution to begin with is extremely low (Table 5). As a result the sequential extraction analyses are not adequate to demonstrate with any degree of certainty that Ra-226 has been co-precipitated. Analysis of the precipitates for residual Ra-226 was not performed for this series of samples.

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